



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improved Process for the Production of Purified Magnesium Carbonate

We, BASIC REFRactories INC., a corporation organised and existing under the laws of the State of Ohio, United States of America, of 845, Hanna Building, 5 Cleveland, Ohio, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the 10 following statement:—

This invention relates to the production of magnesium carbonate from ores containing magnesium oxide, hydroxide or carbonate.

15 On calcining magnesia-providing material, such as dolomite, and hydrating and carbonating in an aqueous slurry, nesquehonite ( $MgCO_3 \cdot 3H_2O$ ) and calcite ( $CaCO_3$ ) are produced. However, the 20 crystallization into discrete grains of magnesium carbonate and calcium carbonate is not always inherently clean, as nesquehonite may contain occluded calcite, calcite may be physically attached 25 to nesquehonite, or nesquehonite may grow into or from an aggregate of calcite, which conditions can lessen effectiveness of separation, and cause a corresponding contamination of the final product.

30 According to this invention, purified magnesium carbonate is prepared from ores containing magnesium oxide, hydroxide or carbonate, by calcining the ore, making a slurry of water and the 35 calcined ore, passing carbon dioxide through the slurry to form a crystalline carbonate of magnesium, separating the crystalline carbonate from the slurry by mechanical means, e.g. froth flotation, 40 making a second slurry of water and the carbonate of magnesium, passing carbon dioxide gas through the second slurry to prepare an alternative crystalline form of the carbonate, and separating the alternative 45 crystalline form from the slurry by mechanical means.

Magnesia material for the process may be dolomite or magnesium oxide or hydroxide rocks, including relatively 50 pure dolomite, impure dolomite, predazzite, pectenite, and impure magnesite. Also, it may be magnesium silicates with

which limestone or dolomite has been fired to give dicalcium silicate and magnesia. The only limitation is that the 55 material must provide a reactive form of magnesia. For conciseness, all such materials are hereinafter referred to as "dolomite".

The raw material is preliminarily 60 crushed, if necessary, and calcined to a suitable temperature. The calcination temperature should not be so high that it makes the magnesia insensitive to reaction, nor should it be calcined so that, 65 on slaking, it forms slimes or colloidal hydroxides. Such slimes are formed on hydration of extremely active material. Usually the temperature should be adjusted to give an incomplete or differential 70 calcination so that all of the magnesium carbonate is changed to the oxide and the major part of the calcite is left undecomposed.

The calcined material is pulverized 75 and mixed with water to form a slurry. The dolomite grains preferably should be just small enough to pass a screen of 200 mesh to the linear inch. The slurry density should be about 4—7 per cent. 80 solids on its calcined basis. This hydration and pulverization may be accomplished by any desired combination of milling and classification used in conventional practice.

The suitably prepared slurry is then treated with carbon dioxide. The concentration of the gas may be such as derived from the calcination operation. A 85 30 per cent. concentration is satisfactory. 90 Certain precautions and procedures may be used to obtain more discrete forms of nesquehonite and calcite. The carbonating may be done at any temperature from about 90° F. down to the freezing point 95 of water and may consume a time from a few hours to several days, and an open system may be employed, as it is generally not necessary to operate under pressure.

100 After treatment, the slurry is subjected to mechanical separation, as for instance froth flotation. With suitably prepared slurry, the flotation is quite simple. All

that is required is a collector to the amount of about 1 pound per ton of solids. The collector may be any one of a number of organic acids or alkali salts of 5 organic acids, of which sodium oleate, sodium palmitate, or sodium naphthenate or their corresponding acids are examples. The collector alone provides an adequate but somewhat brittle froth. A hydrogen 10 ion concentration of about pH 8 is satisfactory for flotation. Under such conditions, the hydrous magnesium carbonate is concentrated in the froth and calcite remains in the tailings.

15 With proper operation along such lines, a product of the following analysis may be obtained, on a calcined basis:

	SiO <sub>2</sub>	0.02 per cent.
	R <sub>2</sub> O <sub>3</sub>	0.21
20.	CaO	14.80
	MgO	84.00

The recovery is about 85 per cent. of the magnesia in the original stone.

Following this first stage of crystallization and separation, the product is subjected to recrystallization according to the procedure to be described. The procedure can best be understood from the fundamental relations between nesquehonite (MgCO<sub>3</sub>·3H<sub>2</sub>O) and lansfordite (MgCO<sub>3</sub>·5H<sub>2</sub>O).

30 Nesquehonite crystallizes in long thin orthorhombic prisms. These prisms may exhibit parallel growth or may even form spherulites radiating from a particle of calcite. Lansfordite crystallizes in the 35 monoclinic system in large blocky or equiaxial crystals. The significance of this is that recrystallization from one state to another produces a profound 40 physical change which may be utilized for purification.

The physical conditions causing either 45 conversion from lansfordite to nesquehonite or the reverse can be accurately controlled. Nesquehonite forms in a fairly broad temperature range of from about 70° F. to 122° F. Somewhere above 122° F. a basic carbonate forms.

50 Lansfordite forms between about 32° F. and 46° F. Between 46° and 70° F. lansfordite or nesquehonite or a mixture thereof may form, depending upon the temperature, the speed of carbonation or 55 the partial pressure of CO<sub>2</sub>. In this range, the formation of lansfordite is favoured by high rates of carbonation or high partial pressures of CO<sub>2</sub> and lower temperatures. Nesquehonite formation

60 is similarly favoured by slower rates of carbonation and temperatures in the higher part of the range of 46° to 70° F. This affords a means of obtaining lansfordite or nesquehonite on original carbonation or of recrystallizing from one

form to another after formation. Also, this may be brought about at a single temperature between 46° F. and 70° F. by change in the partial pressure of carbon dioxide, or it may be brought about by 70 change of temperature, or it can be brought about by change in both the partial pressure of CO<sub>2</sub> and temperature. By forming either lansfordite or nesquehonite and converting one or more 75 times, the impurities entrained in the crystals can be worked down to very low limits.

In practice, it has been found that the conversion of lansfordite to nesquehonite 80 readily occurs in a matter of an hour or two. The conversion of nesquehonite to lansfordite is slower. Both conversions may be speeded and the quality and size 85 of the resulting crystals controlled and improved by seeding, but this is optional. Also, the blocky nature of lansfordite crystals favours a more complete separation than does fine prismatic nesquehonite. Furthermore, the conditions 90 favouring the formation of lansfordite also favour a cleaner product and a faster removal of the magnesia from the residual calcite. Each form of the magnesium carbonate is susceptible to flotation, but may be fouled and rendered non-floatable by other substances, of which magnesium hydroxide is an example.

Usually it is preferred that the crystals be grown as lansfordite. As mentioned, 100 this procedure speeds the reaction, removes the magnesia from the residual calcite faster and to a greater degree and yields a more separable form of magnesium carbonate. The lansfordite is then re-105 moved by flotation from the bulk of the calcite. The froth and the contained solids are then diluted, the temperature raised or CO<sub>2</sub> partial pressure decreased or both, and the lansfordite is converted 110 to nesquehonite and again floated. Ordinarily about a 30 per cent. concentration of CO<sub>2</sub> is applied, and in open or closed system.

The present invention embraces the 115 inversion of either lansfordite or nesquehonite for the purpose of improving the final product or facilitating separation in any way and further embraces any number of such cycles.

As an example: Dolomite from the Niagaran formation in northern Ohio having the following composition:

Ig. loss	47.3 per cent.	125
SiO <sub>2</sub>	0.23	
Fe <sub>2</sub> O <sub>3</sub>	0.057	
Al <sub>2</sub> O <sub>3</sub>	0.065	
CaO	30.3	
MgO	21.2	

was burned to an ignition loss of 18 per 130

cent. It was then pulverised and made up with water to a slurry containing 5 per cent. solids on a calcined basis. The temperature being adjusted to 60° F., a 5 30 per cent. concentration of carbon dioxide was bubbled into the slurry for about 5 hours. Then sodium naphthenate was added as collecting agent, at the rate of 1 pound per ton of solids, and the 10 lansfordite was separated in a flotation-separator from the bulk of the calcite. The lansfordite froth so obtained was diluted with water to about 15 per cent. total solids, the temperature was raised 15 to about 75° F., and carbon dioxide gas as at first was slowly bubbled in for about 3 hours. Then, a collecting agent was similarly added and separation was carried out with a flotation-separator. 20 The segregated magnesia-containing product when calcined analyzed as follows:

SiO <sub>2</sub>	0.01 per cent.
R <sub>2</sub> O <sub>3</sub>	0.1
CaO	7.0
MgO	93.0

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we 30 claim is:—

1. A process for preparing purified magnesium carbonate from ores containing magnesium oxide, hydroxide or carbonate, consisting in calcining the ore, 35 making a slurry of water and the calcined ore, passing carbon dioxide gas through the slurry to form a crystalline carbonate of magnesium, separating the crystalline carbonate from the slurry 40 by mechanical means, e.g. froth flotation, making a second slurry of water and the carbonate of magnesium, passing carbon dioxide gas through the second slurry to prepare an alternative crystalline form 45 of the carbonate, and separating the alternative crystalline form from the slurry by mechanical means.

2. A process according to Claim 1, 50 wherein the first crystalline carbonate of magnesium is lansfordite and the alternative form is nesquehonite.

3. A process according to Claim 1, 55 wherein the first crystalline carbonate of magnesium is nesquehonite, and the alternative form is lansfordite.

4. A process according to any of the preceding claims, wherein dolomite is used.

5. A process according to Claim 4, 60 wherein the temperature of the slurry is adjusted to favour the formation of magnesium carbonate crystals in the form of lansfordite.

4. A process according to Claim 4,

wherein the temperature of the slurry is 65 adjusted to favour the formation of crystals of magnesium carbonate in one crystalline form, the crystals formed are separated from the slurry, and the separated crystals subjected to a different temperature to favour the formation of magnesium carbonate crystals in another crystalline form.

7. A process according to Claim 6, 75 wherein carbon dioxide is bubbled through the slurry and the temperature is adjusted to favour the formation of nesquehonite crystals of magnesium carbonate, a flotation collecting agent is added and the nesquehonite crystals 80 separated from the resultant froth, and wherein the separated nesquehonite crystals are diluted and carbonated and the temperature adjusted to favour the formation of lansfordite crystals, the 85 latter being separated by flotation.

8. A process according to any of Claims 4 to 7, wherein the calcination of the dolomite is controlled to prevent substantial decomposition of the calcium 90 carbonate.

9. A process according to Claim 3 wherein the dolomite is calcined to an ignition loss of about 18 per cent.

10. A process according to Claim 9, 95 wherein the calcined mixture of magnesia and lime is formed into an aqueous slurry containing about 5% solids on a calcined basis.

11. A process according to Claim 5, 100 wherein the temperature of the slurry is adjusted to between 32° and 70° F. so as to favour the formation of the lansfordite crystals.

12. A process according to claim 11, 105 wherein carbon dioxide gas in a concentration of about 30% is bubbled through the slurry of calcined magnesia and lime for a period of about 5 hours.

13. A process according to Claim 11, 110 wherein the temperature of the second slurry is adjusted to about 75° F. so as to favour the formation of nesquehonite crystals, and carbon dioxide gas is bubbled therethrough for a period of 115 about 3 hours.

14. A process according to Claim 7, 120 wherein the flotation collecting agent is sodium naphthenate added in the amount of about 1 pound per ton of solids.

15. A process for the production of purified magnesium carbonate substantially as herein described.

Dated this 26th day of May, 1944.

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